



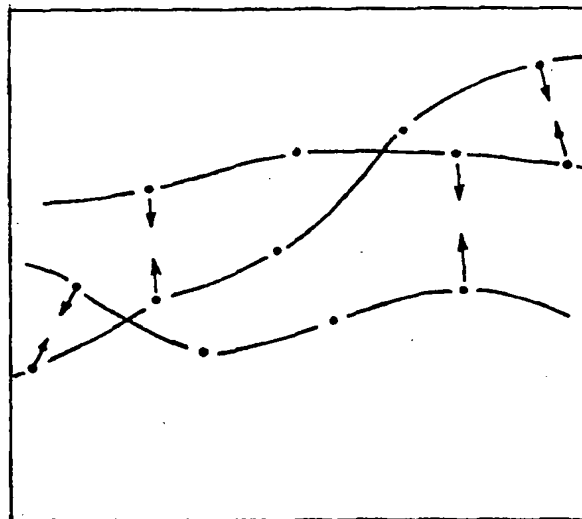
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B05D 3/06	A1	(11) International Publication Number: WO 98/42453 (43) International Publication Date: 1 October 1998 (01.10.98)
<p>(21) International Application Number: PCT/US98/04324</p> <p>(22) International Filing Date: 5 March 1998 (05.03.98)</p> <p>(30) Priority Data: 97104016 24 March 1997 (24.03.97) RU 08/987,266 9 December 1997 (09.12.97) US</p> <p>(71) Applicant: BIOSTERILE TECHNOLOGY INC. [US/US]; 4104 Merchant Road, Fort Wayne, IN 46818 (US).</p> <p>(72) Inventors: IVANOVICH, Batskikh Gennady; Apartment 80, 14 Khimkinsky Boulevard, Moscow, 123364 (RU). ALEXANDROVICH, Vinogradov German; Apartment 15, 12-1 Syrenevy Boulevard, Moscow, 105425 (RU). VLADIMIROVICH, Denisjuck Sergei; Apartment 84, 53 Projezd Shakaloskogo, Moscow, 121221 (RU). IVANOVICH, Klionov Gennady; Apartment 60, 3 Petrovsko-Rasumovsky pr., Moscow, 125083 (RU).</p> <p>(74) Agent: PAPPAS, George; Pappas Law Offices, Suite 300, Harrison Place, 919 S. Harrison Street, Fort Wayne, IN 46802 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	

(54) Title: METHOD OF IRRADIATION OF POLYMER FILMS BY AN ELECTRON BEAM

(57) Abstract

The method of irradiating polymer films by an electron beam comprises a two-stage application of an accelerated electron beam on sections of moving polymer film until the preset radiation dose has been absorbed. The duration of the set time interval between the end of treatment Stage one and the beginning of treatment Stage two of the initially irradiated film is not less than 500 msec. The set dose accumulated by each section of the film in Stage one is sufficient to alter the polymer film material from a free molecular state to a cross-linked state characterized by the formation of 3-dimensional molecular structures having a greater molecular mass.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Method of Irradiation of Polymer Films by an Electron Beam

Area of technology

The invention pertains to the area of radiation technology, specifically to the technology of organic materials radiation modification. It may be used to set up a production line for the manufacture of radiation modified polymer films.

Background of the Invention

At the present time a number of methods are known for irradiating polymer films by electron beam (E-beam) for purposes of organic materials radiation modification.

Thus, for example, there is a method of E-beam irradiation of polyurethane polymers for polyurethane stress relaxation, the E-beam produced by a high voltage accelerator. This method consists in material radiation treatment, the radiation dose ranging up to 12 Mrad as disclosed in E P, A2, 0 204 084, B29C 71/04, published in 1986.

Another E-beam radiation method is used for the removal of residual monomer from wrapper films. This method consists in low energy electron irradiation of the moving film, using a wide exit window with an irradiation dose from 50 kGy as disclosed in DE, A1, 3 602 865, B29C 71/04, published in 1987, accelerating voltage magnitude ranging from 150-300 kV.

The known analogue to the proposed invention is the method of irradiating polymer films by E-beam, which includes treatment of moving polymer film by means of accelerated electrons with an accelerating voltage of 400-750 KeV to effect film

1 crosslinking. The speed at which film moves past the opening of the scanning device is
3.5-5 m/min with a film radiation dose of 10-16 Mrad as disclosed in SU, A, 955 863,
B29C 7104, published in 1982.

5 The drawback of this closest analogue to the invention, as well as the other
analogues mentioned above, is the inefficient energy usage of electrons irradiating
polymer film in order to modify its properties. For single-stage polymer material
irradiation up to full radiation dose, linear molecules crosslinked into a 3-dimensional
structure fail to achieve optimal spatial configuration with the minimum of free energy.
9 A worsening of the physical and mechanical properties of crosslinked polymer film
results.

Brief summary of the invention

13 The basic intent of the invention submitted for patent is to improve polymer
film properties through radiation modification by means of a more efficient usage of
electron radiation energy.

This process result is achieved as follows: in the present polymer film
irradiation method, including the effect of the accelerated electron beam on the moving
17 section of polymer film before preset radiation dose is attained, the dose of radiation is
administered in 2 successive stages. The time interval selected between the completion
of processing stage 1 of each section of film and the commencement of processing
stage 2 of the section of film initially irradiated amounts to no less than 500 msec, and
21 the dose to be absorbed by each section of film during irradiation stage 1 is selected
sufficient to alter film polymer material from a free-molecular state to a crosslinked
state characterized by the formation of a 3-dimensional molecular structure possessing

1 a higher molecular mass.

A time interval equal to one second may be selected.

In the irradiation of polyethylene films it is advisable to select a dose for absorption by the film in radiation stage 1 in the range of 20 to 30 kGy.

5 In order to perform a 2-stage radiation process on moving polymer film it is desirable to utilize an electron accelerator having 2 foil windows for extraction of the electron beam from the accelerator vacuum chamber.

Brief description of drawings

9 The method of irradiating polymer films by electron beam to be patented is elucidated by the following drawings.

Fig. 1. Diagram showing spatial condition of polyethylene molecular structure under initial electron radiation (carbon atoms represented by dots).

13 Fig. 2. Diagram showing spatial condition of polyethylene molecular structure 1 msec after commencement of irradiation (carbon atoms represented by dots).

Fig. 3. Diagram showing spatial condition of polyethylene molecular structure 500 msec after commencement of radiation (carbon atoms represented by dots).

17 Fig. 4. Graph showing the temporal relationship between the change in free energy $\Delta F(t)$ of a polymer system (in relative units of measure) and radiation dose $D(t)$ (in kGy), absorbed by polyethylene film in single-stage irradiation.

21 Fig. 5. Graph showing the temporal relationship between the change in free energy $\Delta F(t)$ of a polymer system (in relative units of measure) and radiation dose $D(t)$ (in kGy), absorbed by polyethylene film in 2-stage irradiation.

1 *Detailed Description of the Invention*

The method submitted for patent of irradiating polymer films includes the following operations:

5 Moving the polymer film to be irradiated in a given direction by means of a conveyor of any known design.

9 Initial treatment (radiation stage 1) by a beam of accelerated electrons on a section of moving polymer film until sufficient radiation dose has been absorbed by the polymer film material to alter it from a free molecular state to a crosslinked state, characterized by the formation of 3-dimensional molecular structures with a higher molecular mass.

13 Follow-up treatment (radiation stage 2) by a beam of accelerated electrons on each previously irradiated section of the polymer film, until preset radiation dose has been fully absorbed, over a time interval no less than 500 msec. in duration.

In this particular example of the application of the invention for radiation modification of polyethylene film the recommended absorption dose for the portion of film in radiation stage 1 is 20 - 30 kGy.

17 The length of the time interval between the conclusion of polyethylene film radiation stage 1 and the commencement of radiation stage 2 is equivalent to 1 second.

21 For polymer material from which film is manufactured by the present method of radiation modification treatment a wide range of crosslinking polymer systems, such as polyolefins, polyacrylates, and other linear crosslinking molecular structures, may be used.

As for the means of providing the two-stage radiation by accelerated electrons of polymer film (in the example under consideration polyethylene) separated by a time

1 interval, any currently known electron accelerator may be utilized.

Thus, for instance, two electron accelerators may be used for the two-stage irradiation of polymer film, placed one after the other over the length of the moving film, with the exit foil windows positioned above the surface of the film sections to be
5 irradiated (see SU, A, 727 087, HO5H 5/00, G2IH 5/00, published in 1983, Fig. 2).

More efficient from the standpoint of conservation of material and energy resources would be the option of using a single electron accelerator constructed so as to permit two-stage irradiation of polymer film US, A, 3 679 930, HOIJ 29/76,
9 published in 1972. In contrast to other types of electron accelerators this accelerator US, A, 3 679 930, HOIJ 29/76, published in 1972 features two foil windows for the extraction of electrons from the vacuum chamber. Placing the accelerator's foil windows above the moving film thus makes possible a sequential two-stage radiation
13 of film with the preset time interval in between.

The invention submitted for patent is predicated on the following experimental and theoretical bases.

Research into the structural changes and properties of irradiated polymer films,
17 based on the example of polyethylene, has made it possible to identify clearly defined stages through which polymer passes as the dose increases.

In the initial radiation stage, at approximately 20-30 kGy, cross co-valence linking occurs between the individual carbon atoms comprising the linear molecules
21 along with generation of 3-dimensional spatial polymers possessing a higher molecular mass. The properties acquired in this stage by the polymer are determined not so much by newly arising rigid bonds/links formed by a ramified molecular system, as by cross-molecular interaction between these systems which makes possible their mutual

1 displacements and deformations in the presence of external mechanical influences.
Under such conditions polyethylene comes to closely resemble in its properties rubber-
like materials.

As the dose increases the density of crosslinking increases and the polyethylene
5 structure is transformed into a unified spatial network. As a result the material
assumes useful new properties: increased modulus of elasticity, increased tensile
strength, resilience to influences of chemicals and temperature.

In the third stage, approximately 300 kGy and above, polyethylene begins to
9 change into a solid glasslike substance of no interest for the film modification process.

The presence of the stages mentioned above in the dose absorption process
offers a basis for investigating the kinetics of the transformations arising in the
individual stages. Polymer material may be viewed as a complex system consisting of
13 two interacting subsystems: electron-chemical and nuclear-molecular, forming a
definite compound structure. It is precisely under these conditions that the non-
inertial electron-chemical subsystem absorbs the irradiation energy and is
instantaneously modified according to the dose absorbed by spatial redistribution of
17 electron links; the inertial nuclear subsystem, however, accepts these changes and
adjusts to them only after a substantial delay.

In a simplified form the response of the polymer system is the consequence of
the following two processes.

21 Fig. 1 shows a displacement of carbon atoms, between which cross-linkages
have arisen, to new equilibrium parameters corresponding to a minimum of energy in
the sector where these cross-linked states are localized. The characteristic relaxation
time of this process has virtually nothing to do with the accumulated dose, though it

1 does depend to a small degree to the structure of the material and is equal to
approximately 1 msec.

Fig. 2 shows a change in the configuration of the molecular chains, tied in with
the minimization of energy in the overall conformation space. This process is initiated
5 following the process of local carbon atom displacements and includes a part of the
structural rearrangement of the system caused by the formation and extraction beyond
the matrix limits of free products of radiolysis, for example, molecular hydrogen during
the irradiation of polyethylene.

9 This part of the structural rearrangement occurs only in radiation stage 1 when
the polymer system is not yet cross-linked and consists of a structure of moveable
ramified polymer molecules (see Fig. 2).

An analysis of the experimental data for cross-linking polymer materials
13 indicates that the structural rearrangement of the system, connected with the effect of
conformational adjustment, last from 500 msec. to 2 sec., depending on external
conditions (temperature, mechanical loads, etc.)

Thus the minimum time from the commencement of irradiation of the polymer
17 film to the conclusion of conformation system adjustment is equal to 500 msec.

When the radiation dose is increased until a fully cross-linked structure of
polymer material is formed (see Fig. 3), the processes connected with conformation
adjustment are practically nonexistent; instead the newly arisen cross-links fix and
21 reinforce the structure formed earlier.

In single-stage irradiation of polymer film the full irradiation dose D_0 is
absorbed much more rapidly than necessary to achieve optimal system configuration
with the minimum amount of free energy F .

1 For example, in single-stage irradiation of polyethylene film with a film
conveyor speed of 10 m/min. across an accelerator foil exit window 0.05 m in width
the exposure time for full irradiation dose D_0 shall be 300 msec. During this time, with
a selected electron beam current value, a preset film irradiation dose of 50 kGy is
5 accumulated (see Fig. 4, curve 1).

The irradiation process may be intensified by increasing the electron beam
current, for instance, by a factor of 3. In this case the preset dose (50 kGy) will
accumulate in 100 msec (see Fig. 4, curve 2). In the example under consideration (see
9 Fig. 4), that of single-stage film irradiation, the dose value (D_{mol}) = 20 kGy
corresponds to the transition threshold of polyethylene from a free molecular state to a
cross-linked state characterized by the formation of 3-dimensional molecular structures
with a greater molecular mass. After the accumulation of the indicated irradiation dose
13 (after 120 msec. for curve 1 and 30 msec. for curve 2 respectively—see Fig. 4) the
process of relaxation of free energy F ceases and the polyethylene is cross-linked into a
spatial structure with residual free energy F , which is greater in proportion to the
intensity of the radiation process (see Fig. 4 where curve 1 relation of $F(t)$ corresponds
17 to curve 1 relation $D(t)$, and curve 2 $F(t)$ to curve 2 $D(t)$).

In the polymer film irradiation method submitted for patent a two-stage
irradiation scheme is used for the cross-linking of polymer systems (see Fig. 5), which
is better adapted to the internal kinetics of the processes.

21 Irradiation stage 1 of this method is concluded by the formation of a ramified
molecular structure (see Fig. 2) under the irradiation dose accumulated over the course
of time interval τ_1 . A dose D_{mol} absorbed by every section of the film in irradiation
stage 1 is selected sufficient to effect the transformation of the polymer material from a

1 free molecular state to a cross-linked state characterized by the formation of 3-
dimensional molecular structures having a greater molecular mass. In the example
under consideration the dose D_{mol} equals 20 kGy.

5 Upon expiration of time interval Δt (after conclusion of stage 1) necessary for
the relaxation of system's free energy F , arising during first irradiation dose D_{mol} ,
irradiation stage 2 follows during time interval τ_2 until total radiation dose has been
absorbed sufficient to effect complete cross-linking of the polymer structure into a
unified spatial network.

9 In order to implement the method submitted for patent the following conditions
must be present to ensure optimal irradiation energy use so as to obtain the specified
properties of polymer film:

$$\Delta t \geq 500 \text{ msec}; R_0 \times \tau_1 \geq D_{mol}; R_0 \times (\tau_1 + \tau_2) = D_0;$$

13 where R_0 = irradiation dose rate (Gy/sec.)

From the relations plotted in the graph (Fig. 5) it can be seen that at the
moment irradiation stage 2 is complete the polymer system has succeeded in dumping
free energy F and by this means has become cross-linked into a more optimal spatial
17 configuration. This phenomenon ensures overall a more efficient use of electron
energy for irradiation and improves the physical and mechanical properties of irradiated
polymer films—an example of the technical result attainable by the invention.

21 The invention being submitted for patent is designed for use in a radiation
production process and may be utilized for the modification of organic materials,
particularly polymer films.

The invention may be used for the development of maximum efficiency

1 production lines for the manufacture of radiation modified polymer films.

A broad range of cross-linking polymer materials may be subjected to radiation, such as polyolefins, polyacrylates, and other linearly cross-linking structures.

1

9

13

17

21

irradiating the moving polymer film with accelerated electrons at a first stage;
irradiating the moving previously irradiated polymer film with accelerated

1 electrons at a second stage; and,

wherein the length of time between the conclusion of the irradiating at stage one and the commencement of irradiating at stage two is not less than 500 milliseconds.

5 6. The method of irradiating moving polymer film of claim 5, wherein the irradiating dose absorbed by the moving polymer film at stage one is sufficient to effect the transformation of polymer film material from a free molecular state to a cross-linked state characterized by the formation of three dimensional molecular structures
9 with a greater molecular mask.

7. The method of irradiating moving polymer film of claim 5, wherein the length of time between the conclusion of the irradiating at stage one and the commencement of irradiating at stage two is not less than 1 second.

13 8. The method of irradiating moving polymer film of claim 5, wherein the irradiating dose absorbed by the polymer film at stage one is between 20-30 kGy.

9. The method of irradiating moving polymer film of claim 5, wherein an electron accelerator with two foil windows for the extraction of the electron beam
17 from an accelerator vacuum chamber is used for providing accelerated electrons and irradiating the polymer film at both said first and second stages.

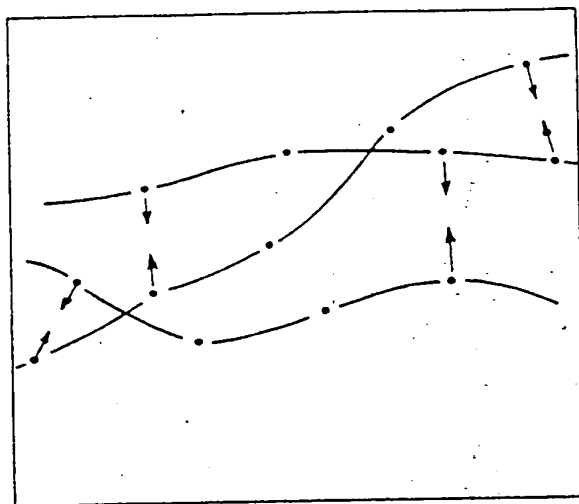


FIG. 1

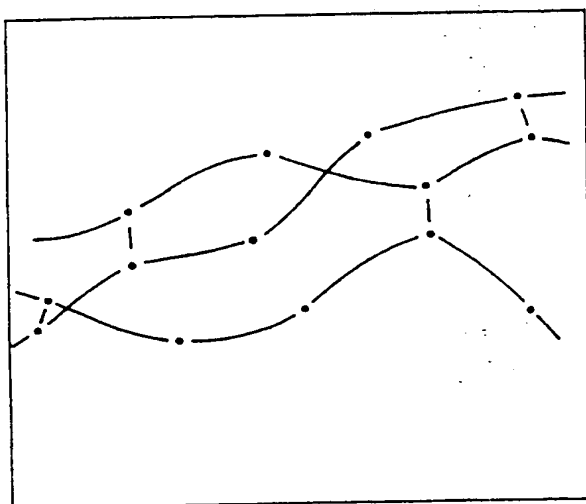


FIG. 2

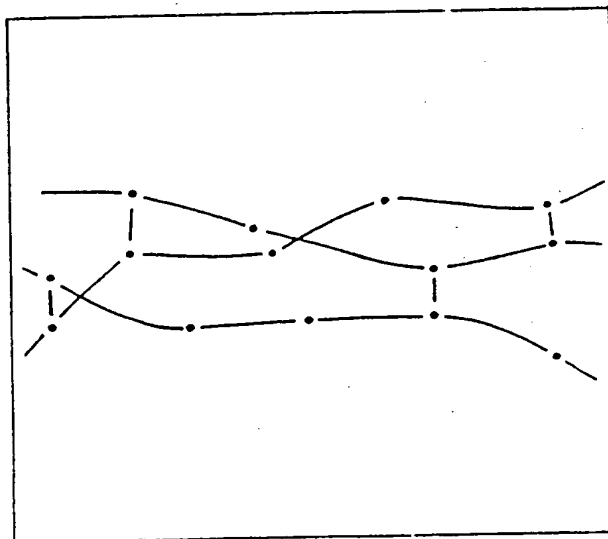


FIG. 3

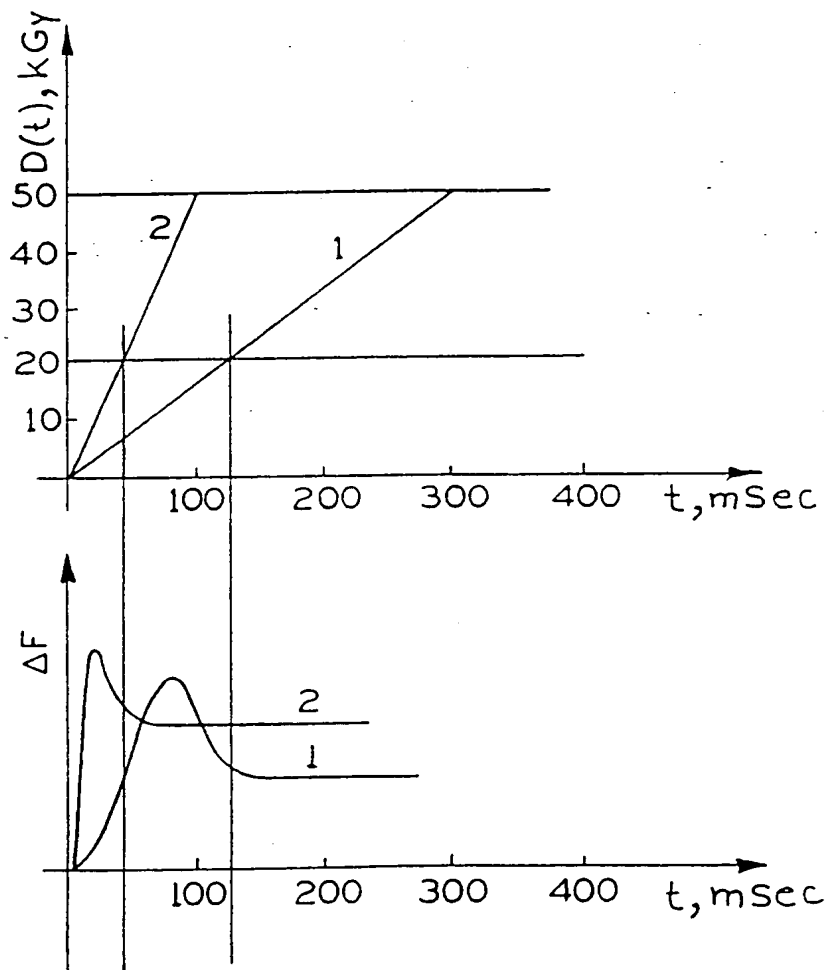


FIG. 4

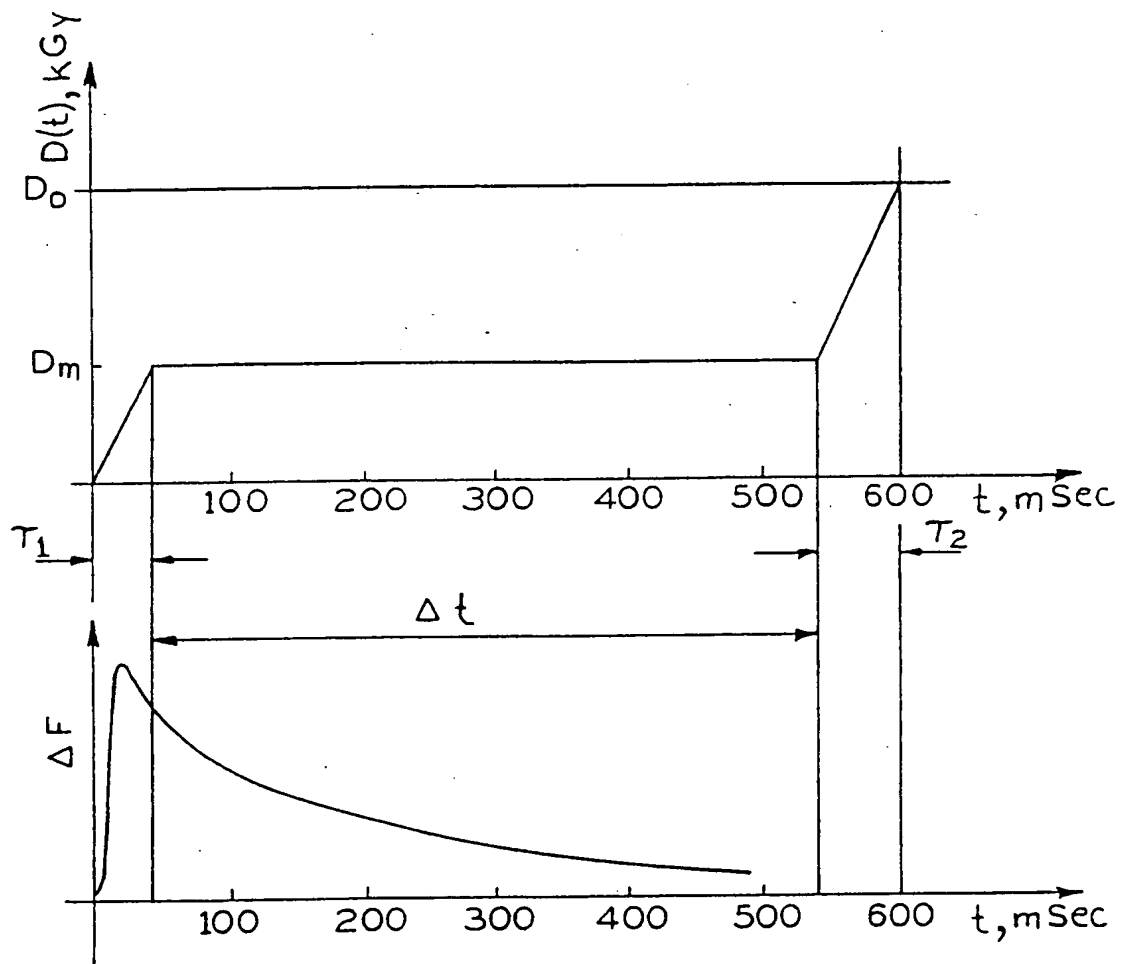


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/04324

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B05D 3/06

US CL : 250/492.3

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 250/492.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,642,244 A (TRIPP et al) 10 February 1987, (10.02.87) whole document, especially col. 3, line 65, through col. 4, line 2.	1, 3-6, 8, 9 ----- 2, 7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 MAY 1998

Date of mailing of the international search report

15 JUL 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JACK BERMAN

Telephone No. (703) 308-4849

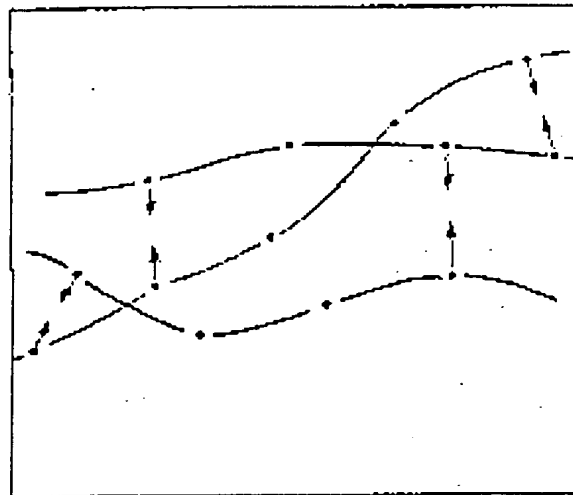


FIG. 1

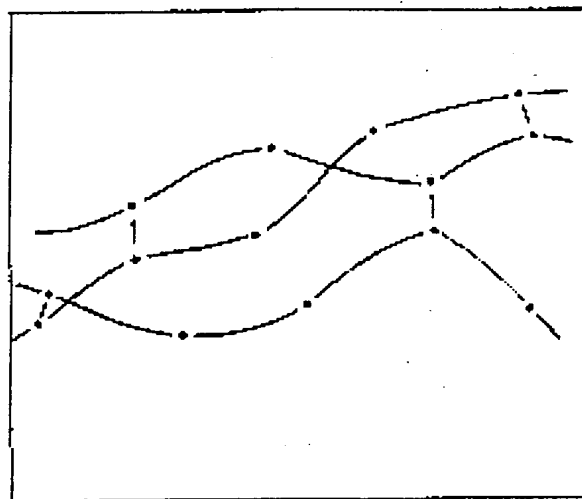


FIG. 2

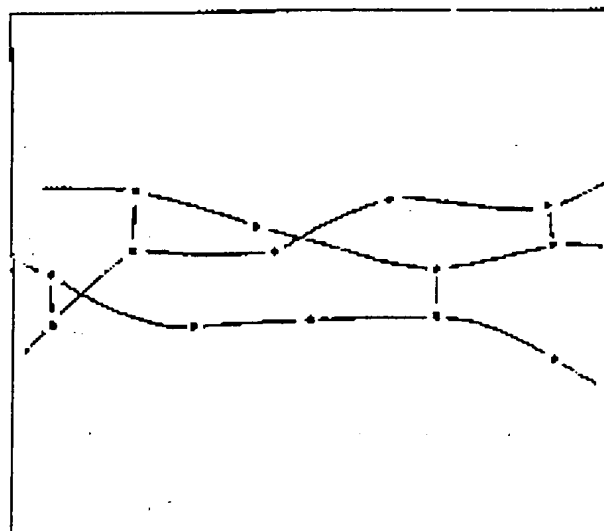


FIG. 3

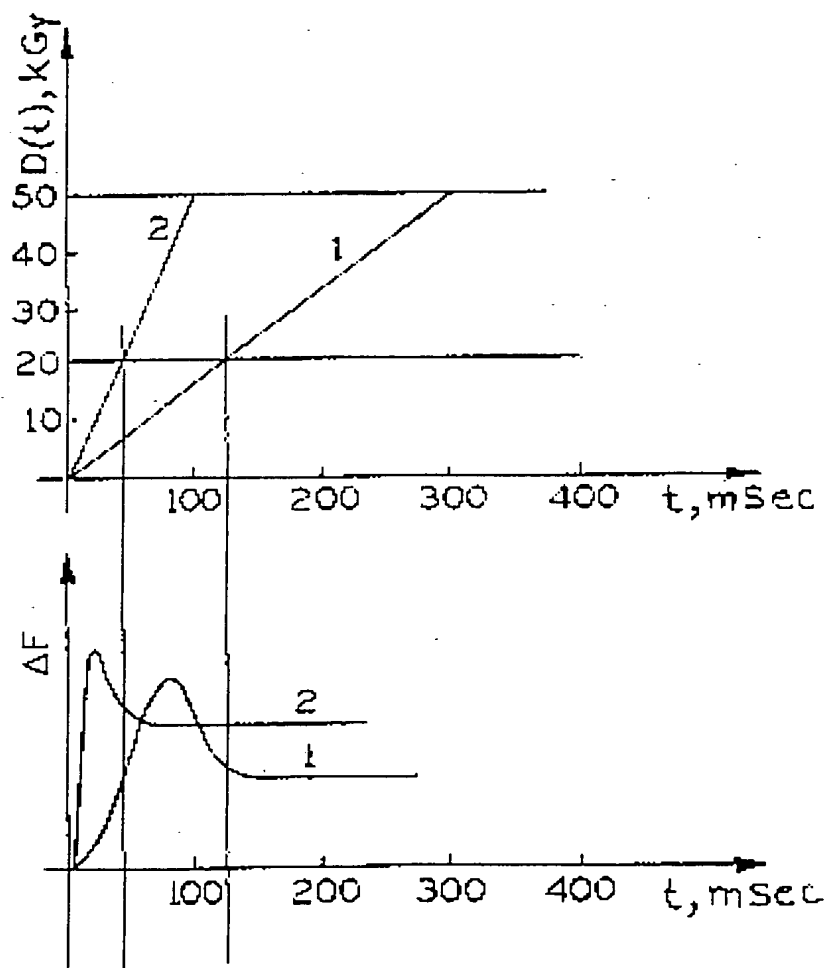


FIG. 4

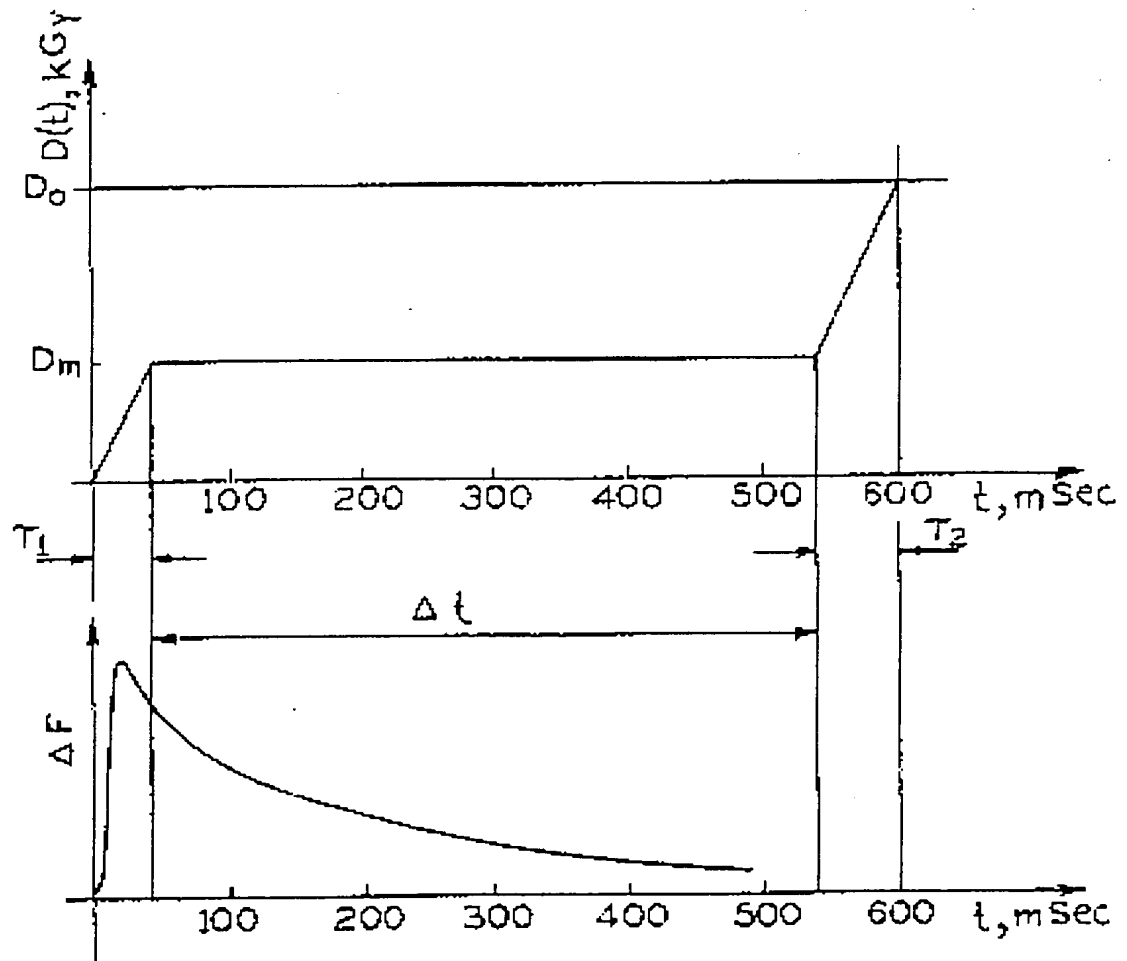


FIG. 5